Nanocomposite Semi-Solid Electrolytes based on Alkoxysilyl Functionalised Iodide and Mesylate Ionic Liquids

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Semi-solid ionic conductors are gaining importance as electrolytes in fuel cells, lithium rechargeable batteries, dye sensitised photoelectrochemical cells and electrochromic devices. For the latter, the commercial breakthrough has been limited by long switching times and insufficient cycling stability, with the electrolyte being recognised as the weakest point of the whole system[1]. The liquid electrolytes were still affected by stability problems, therefore investigations of various polymer electrolytes started, but the devices were limited by low polymeric ion conductivity. Ionic liquids became recognised as the most viable option for the preparation of EC devices due to their wide electrochemical stability windows and good ionic conductivity even at room temperature. Despite their low vapour pressure they are still liquids at room temperature, which actuated the studies of their solidification with addition of either solid nanoparticles or small weight gelators, and also through their incorporation in polymer matrices. Another innovative approach was also synthesis of polymerisable ionic liquids with different polymerisable groups like vinyl, acryl,… positioned either on cations or anions[2]. This approach can be used also in case, when alkoxysilyl functionalised ionic liquids[3] are synthesised, enabling the reactions of solvolysis (hydrolysis) and condensation after their initiation with suitable catalysts like glacial acetic or formic acid.

In this work we will present a series of alkoxyfunctionalised ionic liquids on the basis of imidazolium, either single or bis end-capped, with iodide or mesilate anion. The iodide ones enable the preparation of redox I_3^-/I^- electrolytes that can be applied in hybrid EC devices between optically active WO_3 and catalytic layer of Pt on FTO glass, while mesilate ionic liquids were used for the preparation of classical battery type of EC devices with two intercalation thin films after addition of lithium salt.

Bis end-capped iodide ionic liquid 1,14 bis(3-(3-(3 methoxysilyl)propyl))imidazolium 1-il)-3,6,9 trioxa undecan iodide (MC060) was extensively investigated and its conductivity was improved from ~10^{-4} S/cm to the order of magnitude 10^{-3} S/cm after addition of alkyl functionalised ionic liquid 1-methyl-3-propyl imidazolijev jodid (MPImI). The molar ratio MC060:MPImI up to 1:15 could be achieved when glacial AcOH was used as catalyst. Preparation of hybrid EC devices with electrolyte MC060:MPImI = 1:10 with different amount of iodine showed persistent spectroelectrochemical response even up to 15.000 colouring/bleaching cycles. In-situ micro-Raman spectroscopy was further used to get an insight in the functioning of these devices through the formation/decomposition of I_3^- ions in the near proximity of thin film electrodes. Structural properties of electrolytes were deduced from ^{29}Si NMR and ATR IR spectroscopy measurements.

The search for other possible catalysts, i.e. formic acid, further revealed that when similar ionic liquid 1,29-bis(3-(3-(trimethoxysilyl)propyl))imidazolium-1-il)-3,6,9,12,15,18,21,24 oktaoksaheksacosan dijodid (MC227) with longer poly(ethyleneoxide) chain between two imidazolium rings was used even the molar ratio MC227:MPImI = 1:30 could be obtained. The gels were elastic and possessed good gluing properties when applied between two glass plates.

It should be noted that hybrid EC devices were constructed also from completely solid electrolytes prepared from polyhedral oligomeric silsesquioxanes (POSS) functionalised ionic liquid.

Similar approach as in the case of iodide ionic liquids was used also for mesylate ionic liquids. Therefore, bis end-capped ionic liquid 1,14-bis(3-(3-(3-methoxysilyl)propyl)imidazolium 1-il)-3,6,9 trioxa undecan dimesylate (MC213) was mixed with alkyl-functionalised 1-methyl-3-propyl imidazolium mesylat (MC215) up to molar ratio 1:10 and after addition of lithium salt applied in a battery type of EC devices.

References:

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